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SIXTEN ABRAHAMSSON

Solid state behaviour of long branched-chain fatty acids

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SOLID STATE BEHAVIOUR OF LONG BRANCHED-CHAIN FATTY ACIDS

INAUGURAL DISSERTATION

BY

SIXTEN ABRAHAMSSON
FIL. LIC., VÄRML.

BY DUE PERMISSION OF THE FACULTY OF SCIENCE OF THE UNIVERSITY OF UPPSALA TO BE PUBLICLY DISCUSSED IN THE LECTURE HALL OF THE INSTITUTE OF CHEMISTRY, MAY 23, 1959, AT 10 A.M., FOR THE DEGREE OF DOCTOR OF PHILOSOPHY. IN ADDITION TO THIS SURVEY THE PAPERS NUMBERED 20–27 IN THE LIST OF REFERENCES WILL BE PUBLICLY DISCUSSED.

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Solid state behaviour of long branched-chain fatty acids

By Sixten Abrahamsson

With 12 figures in the text

Introduction

Higher fatty acids with a branched hydrocarbon chain were first shown to exist in nature about 30 years ago when Andersson and his collaborators isolated tuberculostearic acid (1) from the lipids of tubercle bacilli. The acid was later shown to be (−)-10D-methyloctadecanoic acid (2, 3). Other more complicated branched-chain acids are also present in tubercle bacilli (4).

During the last 15 years methyl-branched fatty acids have been found to be fairly common in nature. Weitkamp (5) isolated several acids of the *iso-* and *anteiso-* acid series from wool wax, and Shorland and his co-workers discovered many acids present as trace components in various animal fats (6). However, no simple natural branched-chain acid with a branch larger than a methyl group appears to have been found.

In the production of synthetic fat, branched-chain acids are formed by air oxidation of branched hydrocarbons present in the starting material.

In spite of the biological importance of the methyl-substituted fatty acids, no detailed study of their structure in the solid state has been reported. Surface-film investigations show, of course, an increased area demand per molecule for branched acids in comparison with normal acids. In a series of isomeric methyl-substituted acids the area per molecule is largest when the branch is in the middle of the chain (7, 8). This is a parallel to the melting point lowering which is largest when the branch positions are located about the mid-point of the chain (9, 10, Fig. 5). Although no definite conclusions can be drawn about the side packing and the shape of the molecules in the monolayer, it appears that at least some methyl branched acids have tilted molecules in condensed surface films in contrast to the vertical molecules of normal chain acids (see Stenhagen, 11).

As usual with compounds containing a long hydrocarbon chain, a large amount of X-ray data has been reported for the long-spacings of branched acids, i.e., the perpendicular distance between crystallographic planes with equivalent end groups of the molecules (e.g., for methyloctadecanoic acids Refs. 3, 12–16). Although care is always needed in the structural interpretation of these data, the data indicate that certain branched acids have their carbon chains more tilted towards the end group planes than have the normal-chain acids. This was confirmed by the first more detailed X-ray analysis of a methyl-branched acid. Stenhagen, Vand and Sim (17) determined the molecules of isopalmitic acid to be tilted 43–45° to the (001) planes,

whereas the corresponding value for normal acids is about 60° (18). The analysis gave no clear picture of the branch region, however. Single crystal data have been given by Clark and Chu (19) for the 17- and 16DL-methyloctadecanoic acids and for 14DL-ethylhexadecanoic acid.

In connection with studies of long-chain compounds by S. and E. Stenhagen and their collaborators, it became necessary to extend the knowledge of the structure of these compounds in the solid state. A programme of X-ray structure analysis of such compounds was therefore initiated at this Institute with the primary object to be the determination of the molecular arrangements resulting from the interplay of the packing requirements of the long hydrocarbon chains and of the polar groups and branches.

The first contribution was the study of normal-chain fatty acids by von Sydow reviewed in Ref. (18). A natural extension of this work is the study of branched-chain acids. A fundamental problem of such a study is the effect on the molecular packing of a branching methyl group in different positions along the chain. Therefore in 1954 the present author began a structure investigation of branched acids with special reference to the racemic methyl-substituted octadecanoic acids. The study has also included an investigation of some optically active forms of this series. Branched acids of different chain lengths have been studied only in binary systems containing normal fatty acids. The results of the investigation are given in this paper and Refs. (20–27).

Material used

In the following text *n*-octadecanoic (stearic) acid is called *n*-C_{18}, 14-methyl-pentadecanoic (isopalmitic) acid 14-Me-C_{15}, 14DL-methyloctadecanoic acid 14DL-Me-C_{18} and so on.

Since impurities may change the solid state behaviour of a substance, pure acids are a necessity for a crystal structure investigation.

The complete series of racemic methyloctadecanoic acids was kindly provided by Professor J. Cason and the preparation of these acids is described in Refs. (2, 9, 28–32).

Several of the acids used were synthesized by Professor E. Stenhagen and his collaborators: 14DL-Me-C_{18}, 9DL-Me-C_{18}, 3DL-Me-C_{18}, 3D-Me-C_{18}, 2DL-Me-C_{18} and 2D-Me-C_{18}, characterized in Refs. (15, 16, 22 and 33).

The melting points of the presently known methyloctadecanoic acids are given in Table 3. For data of other acids used, Ref. (26) should be consulted.

Structure determination

The crystal structures have been solved by single crystal X-ray methods. Electron density projections in one direction only, have been sufficient to reveal the molecular packing.

The difficulty in obtaining good single crystals of a long-chain compound for the X-ray work is well known. The crystals are usually very thin and soft, and are frequently twinned or bent. Considerable effort has, therefore, been made to find suitable crystals. The intensity material used for these structure determinations has been good except in one case (22) in which streaky reflexions could not be avoided.

As crystals giving acceptable reflexions in the zero layer might give spots of bad shape in higher layer lines, three-dimensional analysis demands crystals of a quality very rarely found for long-chain compounds.

The hydrocarbon part of a long-chain compound has a strong tendency to adopt a tight side-packing. They most often arrange with a regular or almost regular plane zig-zag conformation. The carbon chain is then periodic with respect to the CH_2 groups, and for a particular chain packing there exists a characteristic subcell describing the translation between equivalent positions within one chain and in adjacent chains. The subcell reveals itself in the reciprocal lattice in which small groups of strong reflexions form the corresponding sublattice.

The subcell concept has been of value in the calculation of structure factors. Müller (34) introduced the concept for this purpose, and later it was fully developed by Vand (35) and Vand and Bell (36). By this method it is possible to calculate, from the few carbon atoms of the subcell, the contribution to the structure factors of all the atoms of the subcell region. Though limited for exact results to compounds with undisturbed chains, e.g. hydrocarbons, it has been used in this investigation in the preliminary stages of some of the structure analyses for phase determination (20–22). In later work the structure factors were exclusively calculated on the BESK computer of the Swedish Board for Computing Machinery.

The dimensions of the subcell can be evaluated from the reciprocal lattice of a long-chain compound. If the dimensions fit the subcell data for a structurally known chain arrangement, it is very likely that this packing exists in the compound. Therefore, it is often easy to obtain information about the principal arrangement of the carbon chains (see p. 70, however). One complication arises when the hydrocarbon part of the molecule is built-up by subcell repetition. If the subcell has a centre of symmetry, it is possible to form different structures depending upon whether $(0,0,0)$ or $(0,0,\frac{1}{2})$ of the subcell is placed at the centre of gravity of the subcell region (cf. 21, 37). Such a shift of subcell origin will not change the amplitudes of the subcell structure factors. Since these are generally the first to be known by sign in a structure analysis and are used for electron density projections, it is possible to obtain good projections for structures with either a difference of $c_s/2$ in the position of the molecules or with a reversed zig-zag of the carbon chains. Precaution is therefore needed to prevent the start of a false structure refinement.

Direct information about the atoms of the molecule that do not belong to the subcell region (i.e., the oxygen atoms and the branch) can be obtained only in special cases. Patterson projections along the shortest axes are dominated by peaks caused by the carbon atoms of zig-zag chain and can only confirm the chain direction found from the orientation determination of the subcell within the main cell. When the carbon chain is severely distorted, however, the subcell reflexions in the reciprocal lattice are not well defined, and the Patterson projection must be used to derive the chain direction.

When it is possible to select reflexions of which the oxygen atoms are the only cause (25, 38), these reflexions can be used for a Patterson projection to give relative oxygen positions. It is then rather easy to suggest a fairly accurate structural model. In other cases, however, the oxygen atoms must be placed in the most probable way in the first trial structure.

The refinement of the atomic coordinates has been accomplished first by the usual method of successive approximations and finally by difference syntheses. It has been necessary to include the hydrogen atoms in the structure factor calculations.

However, their positions have not been obtained from the difference maps, but have been calculated from the standard shape of the CH_2 group determined by Vainshtein and Pinsker (39). In the difference syntheses isotropic temperature factors have been applied in all structures.

Chain packing

The hydrocarbon chains arrange themselves so as to allow the highest possible van der Waals interaction. Generally the chains pack side by side with parallel axes. Several packing modes exist; some of which are energetically equivalent. In some cases a somewhat less favourable packing but still with parallel axes is adopted to fit the structure requirements of parts of the molecule other than the carbon chain.

A radically different chain arrangement is found in compounds in which the interaction between the carbon chains is relatively small in comparison with the forces between the polar groups. Adjacent chains are thus forced to pack with their axes crossed in the lower members of potassium soaps (40), in the A-form of aliphatic normal chain amides (41–43) and in 11-amino-hendecanoic acid hydrobromide (44).

As all the branched-chain acids studied adopt parallel packing modes, only these will be discussed in more detail.

Triclinic packing, T ||

The structure of the triclinic subcell (Fig. 1) was determined by Vand and Bell (36). It contains two CH_2 groups and belongs to the space group $P\bar{1}$. In the correspond-

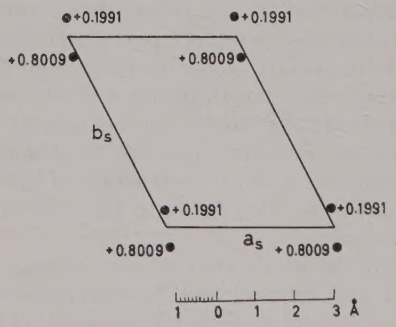

Fig. 1. The triclinic subcell, T ||. After von Sydow (18).

ing carbon chain arrangement, all zig-zag planes are parallel. This chain packing probably exists in the triclinic form of n-hydrocarbons (45) and is also found in the A- and A′-forms of n-fatty acids (18) and in β-triglycerides (36). Most of the methyloctadecanoic acids have this chain arrangement. Subcell data for various compounds are given in Table 1. The values are usually the means of a distorted packing, and therefore the dimensions vary considerably.

Common orthorhombic packing, O ⊥

Analyses of the orthorhombic subcell (Fig. 2) have been performed by Bunn (46), Vainshtein and Pinsker (39) and Shearer and Vand (37). The four CH_2 groups of the cell are arranged according to the space group *Pbnm*. The hydrocarbon chains in this packing have every second chain plane almost perpendicular to the other planes.

Table 1. Data for the triclinic subcell.

Long-chain compound	a_s Å	b_s Å	c_s Å	α	β	γ	Vol./CH_2 Å^3
Trilaurin β-form							
Vand & Bell (36)	4.287	5.40	2.45	74°45′	108°2′	117°24′	23.7
n-C_{15} A′-form							
von Sydow (18)	4.25	5.82	2.61	66°	106°	122°	25.0
n-C_{12}, A-form							
von Sydow (18)	4.42	5.41	2.63	74°	109°	122°	25.0
17-Me-C_{18} (25)	4.28	5.29	2.54	78°	109°	121°	23.3
16DL-Me-C_{18} (21)	4.49	5.40	2.56	73°	107°	123°	24.5
14DL-Me-C_{18} (22)	4.47	5.16	2.57	72°	109°	117°	24.5
9DL-Me-C_{18} (20)	4.20	5.27	2.55	81°	103°	118°	24.2
3DL-Me-C_{18}	4.22	5.18	2.52	75°	107°	119°	22.8
2DL-Me-C_{18} (23)	4.33	5.27	2.50	72°	109°	117°	23.6

The orthorhombic packing is found in a variety of compounds. It, together with the triclinic packing, is adopted by n-paraffins. These two are also the only chain arrangements present in n-fatty acids (18). The only methyloctadecanoic acid studied with this packing was 15DL-Me-C_{18} (Table 3).

Table 2 gives subcell data for some compounds with this packing. The a_s-axis is fairly constant, but the b_s-axis varies considerably. Molecules with short hydrocarbon chains show a rather large value of b_s and, consequently, also of volume per CH_2 group. With increasing chain length these values decrease to that of polyethylene because of the larger interaction along the chains. Degerman and von Sydow (48) have investigated the temperature dependence of the cell dimensions of the B- and C-forms of stearic acid with the orthorhombic chain packing. The b_s-axis was found to increase with increasing temperature, whereas the a_s-axis decreased somewhat (C-form). In this connection it is interesting to note the variation of the b_s/a_s ratio. For the undisturbed packing it is 1.50 but it increases to 1.54 for n-C_{18} (C-form) extrapolated to 70°C and to 1.62 for n-C_{11} (at 23°C, m.p. 28.0–28.4°C). The corresponding value associated with the hexagonal packing of cylindrical rods is

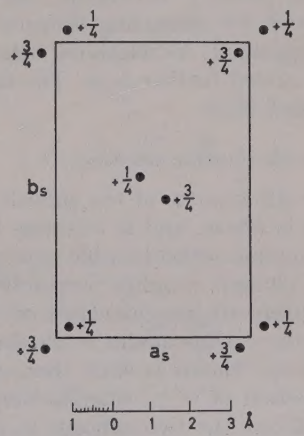

Fig. 2. The orthorhombic subcell, $O \perp$. After von Sydow (18).

Table 2. Data for the common orthorhombic subcell.

Long-chain compound	a_s Å	b_s Å	c_s Å	b_s/a_s	Volume per CH_2 Å^3
Polyethylene					
Bunn (46)	4.93	7.40	2.534	1.50	23.1
n-Paraffins					
Vainshtein & Pinsker (39)	4.96	7.41	2.54	1.49	23.3
n-Hexatriacontane					
Shearer & Vand (37)	4.95	7.42	2.546	1.50	23.4
n-C_{18}, B-form					
von Sydow (18)	4.99	7.40	2.53	1.48	23.3
n-C_{18}, C-form at 23°C					
Abrahamsson & von Sydow (47)	4.96[a]	7.49[a]		1.51	
n-C_{18}, C-form at 70°C (extrapolated)					
Degerman & von Sydow (48)	4.92[a]	7.58[a]		1.54	
n-C_{15}, B′-form					
von Sydow (18)	5.02	7.59	2.51	1.51	23.9
n-C_{12}, C-form					
Vand *et al.* (49)	4.97	7.80	2.52	1.57	24.4
n-C_{11}, C′-form					
von Sydow (18)	4.92	7.95	2.52	1.62	24.7
3 : 1 compound of *n*-C_{18} and 14DL-Me-C_{18}	4.95[a]	7.38[a]		1.49	
Racemic *trans*-9,10-methylene-octadecanoic acid					
Brotherton *et al.* (50)	4.98	8.12	2.60	1.63	27.1
Racemic *cis*-11,12-methylene-octadecanoic acid					
Craven & Jeffrey (51)	5.10	7.55	2.53	1.48	24.4
14-Heptacosanol, Welsh (52)	4.95	7.8	2.58	1.58	24.9
Methyl-branched polyethylene with 8 CH_3-groups per 100 carbon atoms (64)	5.00	7.68		1.53	

[a] Section perpendicular to the *c*-axis.

1.73. Many long-chain compounds adopt a hexagonal structure just below the melting point. It is evident, therefore, that an approach to this hexagonal structure is caused by increasing thermal vibration in the b_s-direction of the orthorhombic chain packing. As relatively little is known about the hexagonal packing, it will not be discussed further here. The large b_s-axes of some other compounds listed will be discussed later.

New orthorhombic packing, O′⊥

The dimensions of the subcell are: $a_s = 7.43$ Å, $b_s = 5.01$ Å, $c_s = 2.50$ Å. Its space group is *Pbnm*, and it contains four CH_2 groups (24). The chain packing resembles the common orthorhombic type with the same subcell symmetry while every second chain plane is roughly perpendicular to the other planes (Fig. 3). The volumes per CH_2 group are also identical in both cases (23.3 Å^3), and means that the interaction along the carbon chains is the same in the two arrangements. The difference in packing of the chains is such that equivalent chains make the closest approach in the b_s-direction of $O'\perp$, whereas they are closest in the a_s-direction of $O\perp$ (Figs. 2 and 3). This allows the two subcells to be identical in shape. Therefore care must be taken

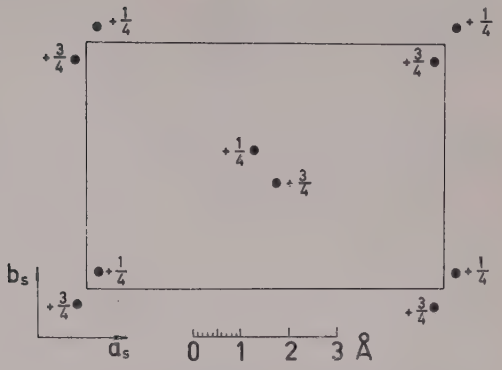

Fig. 3. The orthorhombic subcell, $O' \perp$ (24).

when the chain packing is deduced from subcell dimensions alone. As the symmetry elements of the space group are differently orientated with respect to the identical axes, a distinction between the two types can be made from the extinction rules of the reciprocal sublattice.

Though very simple, $O' \perp$ is unique among the compounds studied and is only found in 2D-Me-C_{18} (24).

New orthorhombic packing, $O \parallel$

Another unusual chain packing was found by von Sydow (53) in (−)-2-methyl-2-ethyleicosanoic acid. The same packing probably exists also in α-sodium stearate hemihydrate (54). The subcell has the symmetry $P2_12_12$ and contains eight CH_2 groups. The dimensions are: $a_s = 8.150$ Å, $b_s = 9.214$ Å, $c_s = 2.551$ Å. All chain planes are parallel in this packing (Fig. 4). The volume per CH_2 group is slightly larger (24.0 Å) than that of the other orthorhombic types for comparable chain lengths. This is compensated by the packing allowing a perfect accomodation of the carboxyl group and the two branches.

Whereas simple long-chain compounds always show the triclinic or common orthorhombic chain packing, other chain arrangements with parallel or ultimately

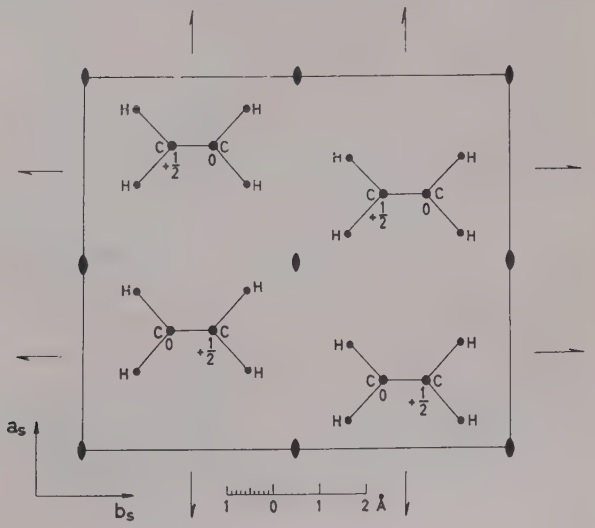

Fig. 4. The orthorhombic subcell, $O \parallel$. After von Sydow (53).

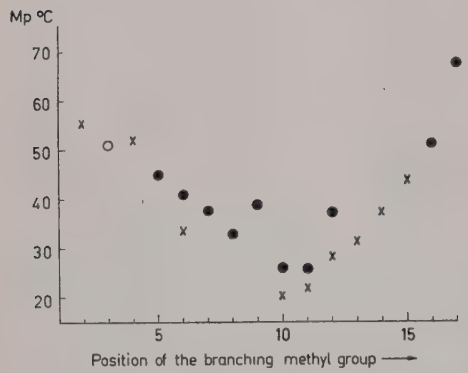

Fig. 5. The melting points of the racemic methyloctadecanoic acids. ● = τ-form; × = ν-form.

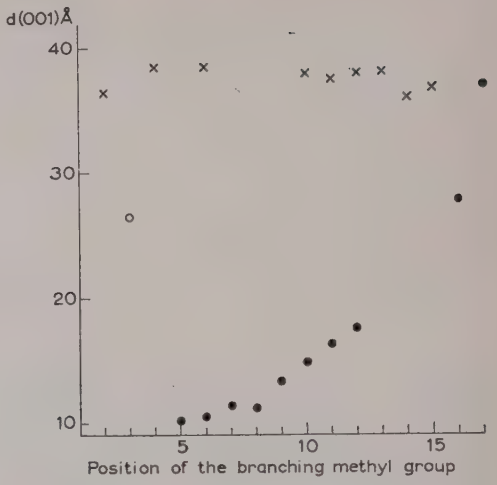

Fig. 6. $d(001)$ of the racemic methyloctadecanoic acids. ● = τ-form, × = ν-form.

with crossed chain axes may be adopted in compounds in which packing considerations of polar groups or branches over-power the hydrocarbon packing. As more complicated long-chain compounds are investigated, new packings of both types will very probably be discovered.

Polymorphism of the racemic methyloctadecanoic acids

During the synthetic work (3, 9, 10) on racemic methyloctadecanoic acids, it was observed that some members of the series existed in two polymorphic modifications. In order to determine the stability ranges and the melting points of the different phases as well as their diffraction patterns, all acids of the series were studied in a continuously recording temperature camera constructed by Stenhagen (55). Their Guinier powder patterns at room temperature were also recorded. The specimens used were obtained by crystallization from various solvents and from the melt. The results are given in Figs. 5 and 6 (and Table 3).

Polymorphism is found for 6DL-Me-C_{18}, 10DL-Me-C_{18}, 11DL-Me-C_{18} and 12DL-Me-C_{18}. In these cases the low melting form is obtained by rapid crystallization from the melt, whereas the other form usually grows from slowly evaporating solvents. Though the structure analyses indicate (see below) that all the acids could exist principally in two forms, only the four acids mentioned have been found to be dimorphous. The pure phases of these acids were difficult to prepare, and in some cases mixtures had to be used (27).

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[a] Cason *et al.* (30)
[b] G. Ställberg (33)
[c] S. Ställberg-Stenhagen (15)
[d] Cason & Winans (9)
[e] Cason *et al.* (31)
[f] Hallgren (16)
[g] Prout *et al.* (2)
[h] S. Ställberg-Stenhagen (3)
[i] Cason & Coad (32)
[j] Cason & Prout (29)
[k] Weitkamp (5)
[l] Cason (28)
[m] Velick (12)
[n] S. Ställberg-Stenhagen (14)
[o] Velick (13)

* The values are not the longest spacings of the acids (see the text).

Table 3. Survey of the methyl-substituted octadecanoic acids.

Methyl-octadecanoic acid	Melting point, °C		d (001), Å			
	Present investigation from DPT diagram (55)	Literature	Present investigation	Literature	Structure type	Chain packing
2DL-Me-C_{18}	55.1	54.6–55.1[a] 55.4–55.7[b]	36.5	37.4[m]	ν	$T \parallel$
2D-Me-C_{18}		54.7–55.0[b]	21.5		(24)	$O' \perp$
		43[b]	36.5		ν	$T \parallel$
3DL-Me-C_{18}	50.7	50.8–51.3[a] 50.7–50.9[c]	26.4	26.5[c]		$T \parallel$
3D-Me-C_{18}		44.0–44.1[c]	26.1	25.9[c]		
		42.8–43.8[c]		36.6[c]		
4DL-Me-C_{18}	52.2	52.6–52.8[a]	38.5		ν	$T \parallel$
5DL-Me-C_{18}	44.3	44.5–45.0[d]	10.2*		τ	$T \parallel$
6DL-Me-C_{18}	40.6	40.0–40.6[d]	10.5*		τ	$T \parallel$
	33.7		38.5		ν	$T \parallel$
7DL-Me-C_{18}	37.5	36.8–37.3[d]	11.4*		τ	$T \parallel$
8DL-Me-C_{18}	34.0	33.9–34.7[e]	11.2*		τ	$T \parallel$
9DL-Me-C_{18}	39.0	38.5–39.1[d] 38.7–39.5[f]	13.3		τ	$T \parallel$
9D-Me-C_{18}		16.4–16.7[f]	13.3		τ	$T \parallel$
		12.5–12.9[f]		44.7[f]		
10DL-Me-C_{18}	25.8	25.4–26.1[g] 25.8–26.1[h]	14.9		τ	$T \parallel$
	20.2	20.9–21.6[h]	37.9	38.5[h]	ν	$T \parallel$
10D-Me-C_{18}		12.8–13.4[g] 12.4–12.8[h]		37.0[h]		
11DL-Me-C_{18}	25.5	26.2[d]	26.3		τ	$T \parallel$
	21.0	21.0[d]	37.5		ν	$T \parallel$
12DL-Me-C_{18}	36.7	36.6–37.1[e]	17.6		τ	$T \parallel$
	27.9	27.6–28.2[e]	37.9		ν	$T \parallel$
13DL-Me-C_{18}	30.7	29.4–31.6[e]	38.1		ν	$T \parallel$
14DL-Me-C_{18}	37.0	37.2–37.6[e] 36.3–36.6 (22)	35.9	35.4[n]	ν	$T \parallel$
15DL-Me-C_{18}	43.8	41.5–43.0[i]	36.8	35.8[m]	ν	$O \perp$
15D-Me-C_{18}		35.2–36.2[i]				
16DL-Me-C_{18}	51.0	49.9–50.6[j]	27.8	28.0[m]	τ	$T \parallel$
16L-Me-C_{18}		46 8[k]		34.2[o]		
17-Me-C_{18}	67.1	67.3–67.8[h]	36.8	36.2[m]	τ	$T \parallel$

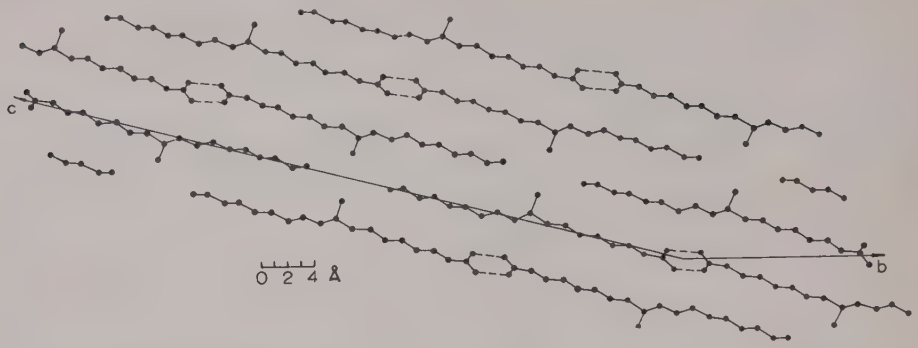

Fig. 7. The molecular arrangement of 9DL-Me-C_{18} as viewed along the shortest axis (20).

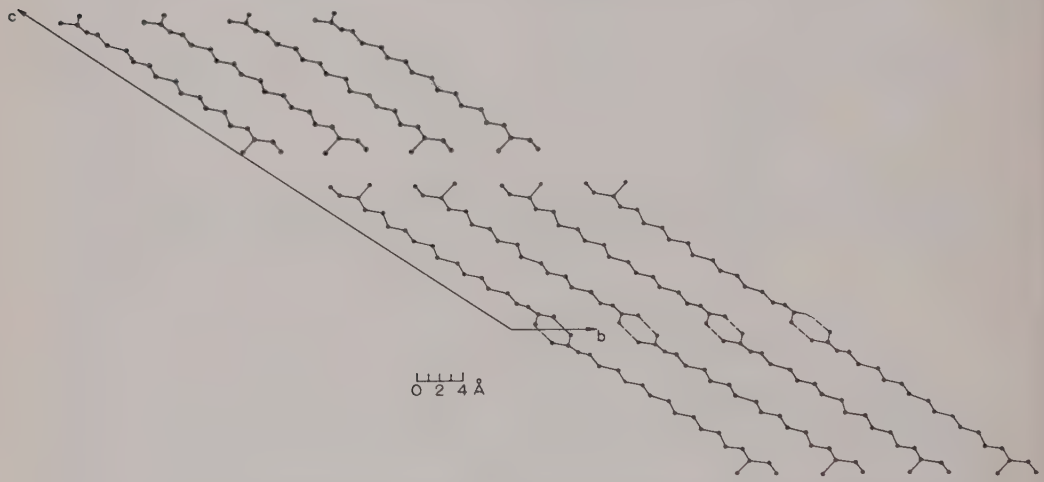

Fig. 8. The molecular arrangement of 16DL-Me-C_{18} as viewed along the shortest axis (21).

From the appearance of Fig. 6 it was tempting to assume that, with the possible exception of 3DL-Me-C_{18} which seems to be unique, two principal modifications exist of these acids: one with the long-spacing varying with the position of the branch (high melting form) and the other with an almost constant value of the long spacing irrespective of the substituent position (low melting form). The validity of this assumption was proved by the following structure analyses.

Structure of the racemic methyloctadecanoic acids

The τ-form with varying long-spacing

Of the acids exhibiting this crystal form, the structures of 9DL-Me-C_{18} (20), 16DL-Me-C_{18} (21), and 17-Me-C_{18} (25) have been determined. The molecular packings are shown in Figs. 7, 8 and 9. The branching methyl groups cannot be accommodated in the chain packing but are given space between the methyl end-groups of the acid

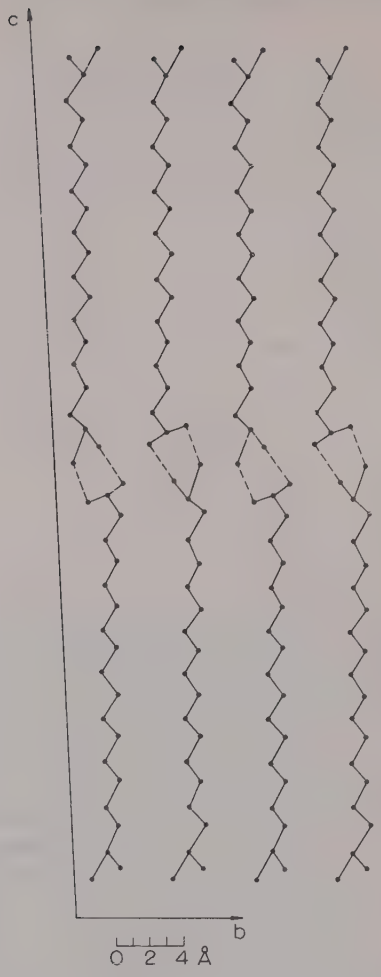

Fig. 9. The molecular arrangement of 17-Me-C_{18} as viewed along the shortest axis (25). The projection direction is inclined about 45° to the plane of the figure.

molecules. Then it is possible for the carbon chains to adopt a tight side-packing, in this case the triclinic. This arrangement has forced a very large tilt on the molecules in comparison with those of normal chain acids. Whereas, the latter have an angle of tilt of about 60° to the (001) planes (18), the most upraised acid in this series, 17-Me-C_{18}, has an angle of tilt of 46°. As the branch is shifted closer to the carboxyl group, the molecules are gradually more tilted. In Fig. 6 this is clearly shown by the $d(001)$ spacings of the τ-form, which decrease successively from the *iso*-acid down to 5DL-Me-C_{18}. It should be noted that the four smallest values given are not the longest spacings of the compounds.

In this arrangement the carboxyl groups have been forced into the chain packing, but they do not fit well and cause distortions. The disturbance is least for the most upraised acid, 17-Me-C_{18}, but is strongly pronounced in 16DL-Me-C_{18} in which the whole packing is distorted (21). The same is expected for other acids of the τ-form. In this connection 9DL-Me-C_{18} is interesting. In the chain direction the carboxyl

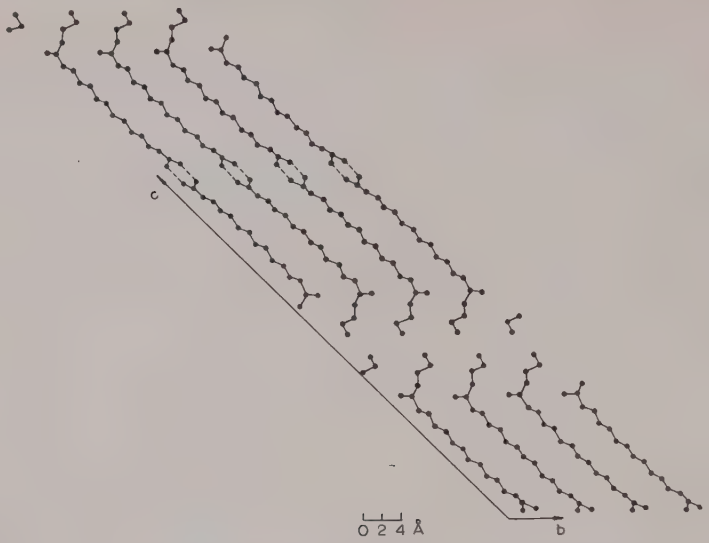

Fig. 10. The molecular arrangement of 14DL-Me-C_{18} as viewed along the shortest axis (22).

groups are here on a level common with the branching atoms and, consequently, also with the chain ends (Fig. 7). The pressure of the carboxyl group on the hydrocarbon chains results in a bending of the neighbouring chains into the space between the chain ends leaving other parts of the chains almost unaffected. The resulting distortions are large, but local, whereas those of other acids are smaller, but disturb the whole chain packing. The effect of these deformations can be inferred from the densities of the acids. The values for 17-Me-C_{18}, 16DL-Me-C_{18} and 9DL-Me-C_{18} are 1.009, 0.998 and 0.991 g cm^{-3}, respectively. The densities thus decrease with the carboxyl groups being forced more and more into the chain packing. A corresponding lowering of the melting points is therefore expected (Fig. 5).

17-Me-C_{18} has a structure in the carboxyl region unusual for long-chain fatty acids. Adjacent carboxyl groups have a slightly different orientation which causes a two-fold superstructure from the chain packing point of view (Fig. 9). Therefore, the atoms of two hydrogen bonded carboxyl groups cannot be coplanar. The planes of the dimerized carboxyl groups in the other acids investigated are parallel, but the planes may be separated as found in α-pimelic acid (56).

The tilt of *iso*-palmitic acid (43–45°) corresponds to that of 17-Me-C_{18}. The structure given (17) is not identical with the τ-form, however. The methyl groups are, in fact, placed into the chain packing. As this has never been found in other pure branched acids, it is likely that the origin of the subcell has been wrongly chosen (cf. above). The correct structure then should be expected to have a reversed zig-zag and be that of the τ-form.

The v-form with constant long spacing

14DL-Me-C_{18} (22) and 2DL-Me-C_{18} (23) are analysed as representatives of this form. Their molecular arrangements are given in Figs. 10 and 11. The shape of the molecule is quite different from that of the τ-form. The branching methyl group constitutes the end of a straight carbon chain starting from the carboxyl group, while the remain-

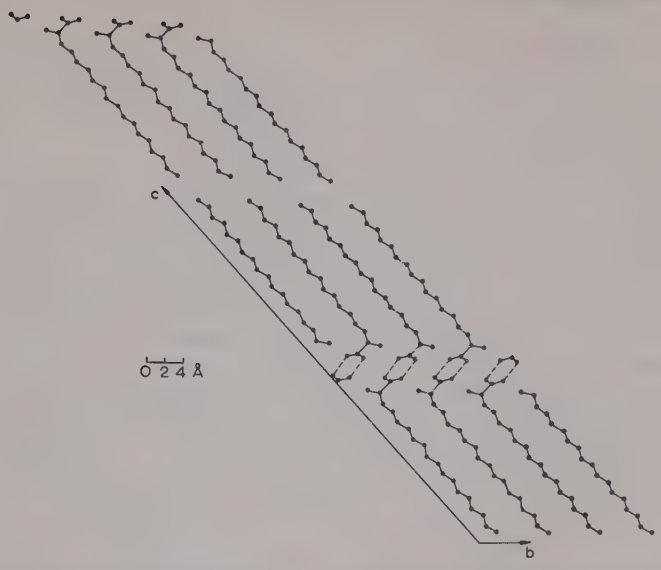

Fig. 11. The molecular arrangement of 2DL-Me-C_{18} as viewed along the shortest axis (23).

ing carbon atoms form a side chain which makes an angle of about 110° with the main chain. As the substituent approaches the carboxyl group, the main chain becomes shorter and the side chain longer. The long-spacing value thereby stays almost constant (Fig. 6). In the case of 14DL-Me-C_{18} the main chain has the triclinic packing, whereas the packing in the side chain region is quite imperfect. When the "side chain" becomes longer, it adopts a tighter packing. In 2DL-Me-C_{18} it dominates and has an almost perfect triclinic packing. The "main chain" here constitutes the branch, in fact. 15DL-Me-C_{18} is somewhat different, since it has the main chains arranged in the common orthorhombic chain packing ($O\perp$).

In the ν-form the molecules have the lowest possible tilt for methyl-branched octadecanoic acids, i.e., approximately that of an *iso*-acid. The disturbing effect of the carboxyl groups is thereby decreased. At the same time, however, an unfavourable packing distortion is introduced in the region where the molecule is branched. The melting points of the ν-acids indicate that the packing is most disturbed when the molecule has two equal chain parts (Fig. 5). Generally, the ν-form represents a less effective filling of space than the τ-form. This can be inferred from the low density of 14DL-Me-C_{18}, 0.95 g cm^{-1} and is consistent with the fact that the ν-form is the low melting modification.

A similar molecular shape with two chain parts making an angle with each other has been found recently in oleic acid by Abrahamsson and Ryderstedt (57) and in racemic *cis*-11,12-methyleneoctadecanoic acid by Craven and Jeffrey (51). In the latter case the volume of the cyclopropane ring is accommodated in a similar way as the methyl group in the ν-form of methyloctadecanoic acids. The smaller volume demand of the ring is revealed by the lower tilt of the main chains in racemic *cis*-11,12-methyleneoctadecanoic acid (about 58°) in comparison with those of the ν-form (about 41°). The angle between the two chain parts seems to be somewhat larger (118°) than in the ν-form (110°). The chain packing in racemic *cis*-11,12-methyleneoctadecanoic acid is the common orthorhombic type (Table 2).

The structure of 3DL-Me-C_{18}

It is apparent from Fig. 6 that 3DL-Me-C_{18} does not fit into the τ- and ν-series. The unit cell is triclinic and contains four molecules: $a = 8.06$ Å, $b = 10.05$ Å and $c = 27.35$ Å; $\alpha = 100°24'$, $\beta = 95°18'$ and $\gamma = 114°30'$.

The subcell first derived was pseudo-monoclinic with $a_s = 8.17$ Å, $b_s = 10.05$ Å and $c_s = 2.52$ Å, $\gamma_s = 116°$. This proved, however, to be a section of the triclinic packing perpendicular to the chain axes, and from the data the usual triclinic subcell (Table 1) could be derived. Space considerations show the molecule to be the ν-type, i.e. to consist of a hydrocarbon chain with a carboxyl acid branch in position $(\omega - 1)$. Whereas 2DL-Me-C_{18} forms double molecular layers (Fig. 11), 3DL-Me-C_{18} apparently has carboxyl groups in each end group plane somewhat like 2D-Me-C_{18} (Fig. 12).

In the infrared spectral studies of methyloctadecanoic acids (27), polymorphism of 3DL-Me-C_{18} was observed. The KBr pellet that contained the acid gave two different spectra depending upon whether it was investigated immediately or a few days after the pressing. Only by extremely rapid cooling (solid carbon dioxide) of the melt could samples be obtained that gave an X-ray powder pattern of another form, but the pattern was too imperfect to allow structural conclusions to be drawn.

Structure of some optically active methyloctadecanoic acids

The high melting form of 3D-Me-C_{18} (Table 3) is interesting since it shows two subcell directions in the structure. The unit cell is monoclinic with eight molecules: $a = 8.92$ Å, $b = 52.2$ Å, and $c = 9.93$ Å, $\beta = 123°$. The following subcell was evaluated from one set of strong reflexions in the reciprocal lattice:

$$a_s = 5.18 \text{ Å}, \quad b_s = 8.92 \text{ Å}, \quad c_s = 2.70 \text{ Å};$$
$$\alpha_s = 133°, \quad \beta_s = 73°, \quad \gamma_s = 129°.$$

These data do not fit with those of any known subcell. A comparison of the Weissenberg photographs with those of the β- and β'-monoglycerides which are being investigated in this Institute by K. Larsson show similarities in the distribution of the reflexion groups corresponding to the subcell. It has been found by K. Larsson that the intensity distribution of the subcell reflexion groups is consistent only with a structure containing monomolecular layers within which, the chains pack with parallel axes. The molecules have opposite tilt in adjacent layers. The chain packing is not yet known in detail. The arrangement in the carboxyl region causing this chain arrangement of 3D-Me-C_{18} is uncertain. The low melting form of the acid found by Ställberg-Stenhagen (15) has not been obtained in a pure state.

The molecular arrangement of the high melting form of 2D-Me-C_{18} (24) is shown in Fig. 12. The carboxyl group branches are accommodated between the ends of the molecules. The carbon chains have adopted the unique packing $O' \perp$ mentioned previously. Another interesting feature of the structure is the hydrogen bond system. Although most methyloctadecanoic acids probably are dimerized, 2D-Me-C_{18} has infinite helices of hydrogen bonds through the structure parallel with the b-axis. The head-to-tail arrangement of the molecules together with the packing $O' \perp$ and the hydrogen bond system allows a very effective molecular packing. This is revealed by the density 1.015 g cm^{-3}, the highest value hitherto found for branched acids. Similar hydrogen bond systems have been found in formic acid (58), acetic acid (59) and in (−)-2-methyl-2-ethyleicosanoic acid (53).

Fig. 12. The molecular arrangement of 2D-Me-C_{18} as viewed along the shortest axis (24).

The low melting modification of 2D-Me-C_{18} has a structure very similar to that of 2DL-Me-C_{18} (space group $P\bar{1}$) as can be seen by the two, almost identical powder patterns. A centre of symmetry cannot be present in the structure of the optically active form, however, which thus belongs to the space group $P1$.

Hallgren (16) reported polymorphism of the optically active forms of 9-Me-C_{18}. In that case the high melting form gave a powder pattern very similar to that of the racemic acid. Here, too, the structure of one polymorph of the optically active acid resembles the structure of the racemic acid. Neither the low melting form nor the remaining optically active forms listed in Table 3 have been studied further.

Structure and physical properties of the crystals

It was mentioned earlier in this paper that the crystals of the methyloctadecanoic acids are usually thin plates which show twinning and deformation. This is consistent with their structures. In the ν-form carboxyl group contact layers alternate with methyl group contact layers throughout the structure (Figs. 10 and 11). This is also the case with the most upraised acids of the τ-form (Figs. 8 and 9). The van der Waals forces in the methyl group contact layers are weak and cause the well-developed (001)-faces of the crystals and the easy cleavage along the (001)-planes. The common twinning on these planes is thereby also explained.

When the molecules in the τ-form become more tilted, the comparatively strong interaction between the carbon chains (cf. 18) will have a large component perpendicular to the methyl group contact layers. No layers of weak forces are then found in the structure; the crystals become harder and do not show a flaky appearance or twinning (cf. 9DL-Me-C_{18}, Fig. 7). For the most tilted τ-acids the methyl group contact layers and the carboxyl group contact layers are very close to each other. This corresponds to a head-to-tail arrangement of the molecules somewhat as shown by the high melting form of 2D-Me-C_{18} with contact layers containing both

methyl and carboxyl groups (Fig. 12). The crystals of this latter form are rather large and lath-shaped. As expected, the longest direction of the laths coincides with the direction of the hydrogen bond helix (24).

Infrared absorption

The infrared absorption spectra between 3500 and 700 cm^{-1} of the crystalline methyloctadecanoic acids have been determined and correlated with the structure data (27).

The band progression between 1180 and 1330 cm^{-1} is disturbed by a substituent along the chain (60). This effect overpowers the possible influence of the τ- and ν-forms on the band progression. Characteristic differences between the infrared spectra of the two forms are not found.

The CH_2 rocking vibration at about 720 cm^{-1} has been suggested (61) to be useful in determining the chain packing. It seems likely that two peaks of equal intensity are associated with a strictly perpendicular orientation of the planes of the carbon chains packed with parallel axes, whereas a parallel orientation of the planes gives a single strong peak. As a deviation from these arrangements might cause gradual transitions between the two appearances mentioned and since the chain packings presently known are numerous, no conclusions can be drawn from the absorption bands in the 720 cm^{-1} region about the exact chain packing in a crystalline long-chain compound.

Binary systems of methyl-branched acids and normal acids

It is known that binary systems of *iso*- or *anteiso*-acids and normal fatty acids show compound formation (5, 62). This is also the case for acids branched farther away from the methyl end of the molecule (26). The molecular compounds have been investigated by X-ray powder methods, and structural information of the phases has been obtained by use of the results from the study of the pure components.

When the number of carbon atoms in the normal acid is smaller than the number of the carbon atom bearing the branch, 1:1 compounds are found (e.g. between 14DL-Me-C_{18} and n-C_{13}). With longer normal chain acids the molecular compounds formed contain 25 mole per cent of the branched acid.

In the 1:1 compounds the carbon chains are arranged in the common orthorhombic chain packing ($O\perp$), and the methyl groups are accommodated between the ends of the short normal chain molecules. This is apparent from the long spacings of 23-Me-C_{24} (47.6 Å) and the 1:1 compound between 23-Me-C_{24} and n-C_{19} (dimorphous: 52.4 and 58.4 Å). The large tilt of the chains of the pure *iso*-acid is not necessary for the accommodation of the methyl groups in the molecular compound since the normal chains do not reach the branch. The tilt of a 1:1 compound resembles, in fact, that of a normal fatty acid. The long spacings of n-C_{24} in C- and B-forms are 52.4 Å and 57.8 Å respectively, and fit well with the spacings given above for the molecular compound.

The 1:3 compounds also have the same chain packing ($O\perp$), but the methyl groups have been forced into the chain packing. This is shown by the 1:3 compound of 14DL-Me-C_{18} and n-C_{18} which has a powder pattern very similar to that of pure n-C_{18} in C-form. The cell dimensions were obtained from the Guinier powder diagram,

and the a_s and b_s subcell axes were calculated to be roughly the same as those of n-C_{18} in C-form (Table 2). Since the orthorhombic packing is tight and no expansion was observed in the subcell dimensions, the methyl group must be assumed to be accommodated only by means of severe local deformations in the branch region. The fact that no molecular compounds are formed between 5DL-Me-C_{18} or 2DL-Me-C_{18} and n-C_{17} (63) may depend on the fact that such deformations cannot appear close to the carboxyl group.

Although the methyl groups in pure branched-chain acids cannot be accommodated in the chain packing, this can be accomplished if the structure becomes poorer in branches by the inclusion of molecules of a normal acid. Similarly the chain packing in polyethylene (64) can provide space for a limited number of methyl branches (Table 2). A group having a smaller volume than that of a methyl group can be accommodated in the chain packing, however, even in the pure compound. In racemic *trans*-9,10-methyleneoctadecanoic acid, the cyclopropane ring is accommodated in a structure resembling that of a normal acid (50). No large local distortions are found, but the whole orthorhombic chain packing, $O\perp$, has expanded in the b_s-direction as shown by the very large b_s-value of 8.12 Å in Table 2. A quite analogous accommodation is found in 14-heptacosanol (52) in which the OH-groups find sufficient space in a regular packing, $O\perp$, with an elongated b_s axis (7.8 Å). It should be remembered that the largest expansion of the chain packing, $O\perp$, caused by thermal vibration is in the same b_s-direction (48). Thus both rise of temperature and branching cause the chains to approach a hexagonal arrangement. The large b_s-values of the shortest n-fatty acids are due partly to thermal and partly to carboxyl group expansion of the chain packing.

SUMMARY

A crystal structure investigation of methyl branched fatty acids has been performed with special reference to the racemic methyloctadecanoic acids.

Two principal arrangements are found for the accommodation of the methyl branch. In the τ-form the molecules have a smaller angle of tilt than those of normal chain acids to allow the branches to be accommodated between the methyl group ends of the long chains of the molecules. The angle of tilt gradually decreases as the substituent approaches the carboxyl group. In the ν-form the methyl group is a part of the straight carbon chain starting from the carboxyl group, and the remaining carbon atoms constitute a side chain which makes an angle of 110° with the other chain. The resulting packing is generally less effective than that of the τ-form. In cases in which the same acid can appear in both forms the ν-form has a lower melting point than the τ-form.

The parallel packing modes of hydrocarbon chains are discussed. Whereas the methyl groups are never accommodated in the chain packing of a pure branched acid, these groups can be forced into the packing if the structure becomes poorer in branches, e.g., by admixture of normal acids.

The infrared absorption of the methyloctadecanoic acids is correlated with the structure data. The study of the CH_2 rocking vibration at about 720 cm^{-1} includes all known parallel packing modes.

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